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PHOTOCHROMIC PROCESS IN COPPER-HALOID GLASSES

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The induced absorption spectra and their relaxation, including the behavior of the spectral dip in the exciton band range, are analyzed. A model is proposed for photochromy as a process of the formation of pair defects of CuCl microcrystal and radiation color centers in the glass matrix on both sides of the microcrystal – glass boundary.

Among recent technological achievements is the development of a production technology for photochromic copper-haloid sheet glass [1, 2]. At the same time, the nature of the colorant phase in this glass remains the subject of discussions, and without this understanding, it is difficult to hope for the improvement of such parameters as darkening intensity of photochromic glass and its spontaneous decolorization duration.

The most common concept assumes the existence of a colloid copper shell, which is formed around the active phase microcrystal under UV radiation and dissociates after the end of UV treatment [3]. Some researchers attribute the spectra of colloid copper to this shell (although there is no certainty with respect to these spectra), or else interpret the induced pigmentation centers as a result of light diffusion on metal spheroids, not taking into account the distribution of spheroids by size and eccentricity. It remains unclear how such a shell can resolve within a few minutes at room temperature. Other authors [4] explain the photochromic effect by the formation and disintegration of various types of point defects in microcrystals (MC) of the active phase without participation of the glass matrix. In this case, the types of defects remain unknown to the authors, except for Cl_2^-, and therefore, the respective absorption bands are derived by these authors from the conditions of formal decomposition of spectra.

The research on the behavior of the fine structure of the absorption spectrum of these glasses (i.e., the exciton bands) performed by us [5] makes it possible to suggest a new model of the photochromic process. This fine structure of the absorption spectrum is primarily manifested in the sensitivity spectra of photochromic glass to the light of different wavelengths.

To determine the sensitivity spectra, we used the following method. Glass samples 1 – 3 mm thick were colored for 30 min using a DRSh-250 stationary mercury lamp, whereas a relatively narrow spectral interval was isolated from the radiation spectrum of this lamp, employing one of nine combinations of standard glass light filters. The maximum in the band isolated by the light filters correlated with the induced optical density in the band 16,000 cm^{-1} divided by the relative value of the calculated absorbed light flow. The dependence averaged for 7 samples of different glasses is shown in Fig. 1.

The above-described method for determining the sensitivity spectrum cannot be regarded as perfect; however, it enabled us to distinguish three specific sensitivity ranges with the following photon frequencies: from 28,000 cm^{-1} and above, 25,000 – 28,000, and 22,000 – 25,000 cm^{-1}. The comparison of the sensitivity spectrum with the glass absorption spectrum before irradiation (Fig. 1) suggests that the medium sensitivity range is determined by the absorption of CuCl microcrystal with the typical narrow exciton band $Z_{1,2}$ having a peak near 26,850 cm^{-1} and a less intense exciton band Z_3 with a peak near 26,300 cm^{-1}. It is precisely the presence of these peaks in the spectrum that determines the sensitivity peak near 26,000 cm^{-1}. The distinctive feature of the low-frequency sensitivity range is the fact that it is not
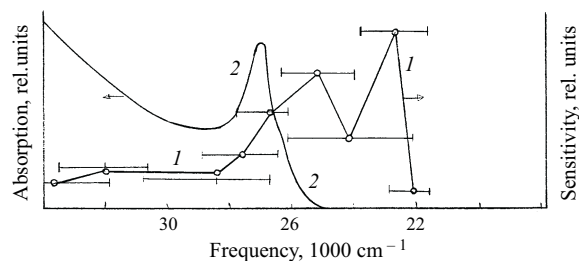

Fig. 1. Copper-haloid photochromic glasses: *1*) spectral sensitivity (horizontal segments indicate half-width of transmission bands of respective combinations of light filters through which the glasses are radiated; the dependence is averaged for 7 samples of different glasses); *2*) glass absorption spectrum.

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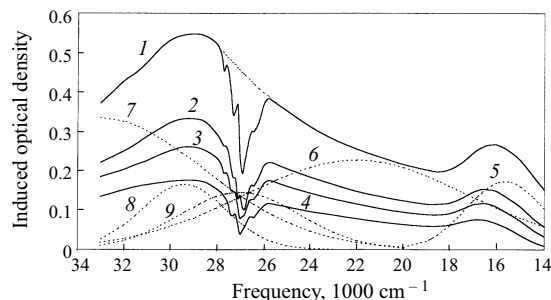
Fig. 2. Spectra of UV-induced additional absorption in photochromic glass 0.25 min (*1*), 8 min (*2*), 14 min (*3*), and 25 min (*4*) after the end of UV radiation. Dashed lines indicate the Gaussian bands of glass RCC (*5 – 7*) and chlorine defects in CuCl microcrystal (*8, 9*).
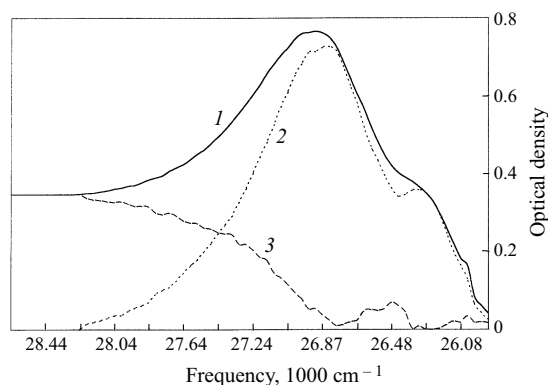
Fig. 3. Arbitrary scale comparison of absorption spectrum intensities of glass (*1*) and the exciton dip (*2*) isolated from the spectrum in Fig. 2, as well as the difference (*3*) between spectrum (*1*) and spectrum (*2*) corresponding to the interzonal absorption spectrum of CuCl microcrystal.

perceptible in all glasses and it correlates with the low-density non-structured edge of the glass absorption spectrum. The transparency of glass in this particular spectrum range facilitates the uniform activation of glass across the sample thickness. The thicker the glass, the more significant the role of this range. In contrast, the high-frequency sensitivity range is the region in which the absorption of the glass matrix rapidly increases with increasing frequency. Therefore, radiation within the specified range activates the glass only inside a thin layer, and its effect is weakly related to the glass thickness.

The exciton bands are manifested in a curious way in the induced absorption spectra. These spectra were measured at room temperature in a wide frequency interval on samples ranging from 0.1 to 2.0 mm thick using a SPECORD M-40 spectrophotometer. It should be noted that measurements of induced spectra have deluded many researchers. Thus, it is stated in [3] that the maximum near 365 nm slightly increases under the glass pigmentation. The fact is that this phenomenon does not mean that the band responsible for the

specified peak is increased, which is partly implied in [3]. On the contrary, as it happens, a dip arises in the range of the exciton peaks (Fig. 2) on the background of the wide bands of the differential spectrum (the difference between the spectra in the tinted and the initial states is registered by the spectrophotometer). This dip is only visible in the differential spectrum, whereas in the tinted glass spectrum it appears that the exciton peak has become more intense. The dip can be isolated from the spectrum in Fig. 2 and compared with the initial absorption spectrum (Fig. 3). The comparison demonstrates that the dip is constituted by two exciton bands, and the difference between spectra *1* and *2* in Fig. 3 represents the interzonal absorption spectrum of CuCl microcrystal (spectrum *3*).

Thus, the photochromic process is accompanied by a decrease in the intensity only of the exciton bands in the absorption spectra. If the model of a metallic copper shell were true, such shell would cover the MC and cause a dip in the shape of the spectrum *1* (Fig. 3).

Additional arguments against the model implying the formation of a metallic shell arise, as a consequence of the analysis of the composition of the spectrum in Fig. 2. We attempted to compose the induced spectrum from the bands of the well-known radiation color centers (RCC) of sodium-silicate glasses and the bands of two MC radiation defects, namely, Cl_2^- and Cl_2^0 [5]. After a slight correction of the peak positions and the half-width of these bands, we obtained good convergence of the summary spectrum with the one observed in the experiment; the divergence does not exceed $2.5 – 3\%$. No space remains for the shell spectra. Note that the radiation coloring spectra of alkaline-borate glasses are not suitable for such modeling. This is presumably an indication of the site in the glass where the MC are formed. Furthermore, the spectrum shown in Fig. 3 does not have any evidence of the presence of other MC, apart from CuCl. Consequently, as the result of heat treatment, CuCl microcrystals are formed in glass, which are sufficiently perfect for the excitons to exist in them (the exciton radius for a large CuCl crystal is 6.5 Å). Microcrystals of the solid solution type are not formed, and no other possible MC, such as $CdCl_2$ or CuBr, are in any way revealed in the investigated process.

By writing the sequence of spectra (Fig. 2) varying in the course of glass decolorization, it is possible to determine the relaxation rate for each of the spectral components comprising the spectrum, including the exciton dip as a separate component. All components relax obeying the same law, whereas the ratio of the maximum rate (for the band $16,000$ cm^{-1}, which determines the tinting in the visible spectrum) to the minimum rate (for the exciton dip) is equal to about 3.5, i.e., the processes of relaxation of all spectral components are probably interrelated, and the respective centers are located near each other.

All the above makes it possible to describe the photochromic process in copper-haloid glasses in the following way. Under the effect of UV radiation, electron-vacancy

pairs and excitons are formed in CuCl microcrystals. The vacancies become occupied by the MC defects Cl_2^- and Cl_2^0, and the electrons migrate toward the MC – glass boundary and form RCC of the electron type in the glass. The surface states of the MC are presumably responsible for the low-frequency range of spectral sensitivity (Fig. 1). The high intensity of pigmentation in this range can be accounted for by the small trapping distances, since the RCC precursors are arranged right near the phase boundary in glass, and the carriers actively migrate along the boundary from the side of the MC. At the same time, the surface states should be sensitive to the impurities localized near the boundary. This is probably the reason for the fact that the spread in the sensitivity values for glasses of various compositions in this range is the most significant.

The above scenario of the formation of RCC and defects near the MC – glass interface determines the spontaneous decolorization of the glass after the end of UV radiation. If the same glass were radiated within the x-ray range, the same RCC would be formed in the glass (although with slightly different ratios of absorption band intensities), but they would not relax at room temperature.

According to our estimates, the average MC radius is about 25 Å. We estimated that 20 – 30 RCC are formed at the border of one MC activated by UV radiation and approximately the same number of Cl_2^- and Cl_2^0 defects are formed inside the MC. As for such defects as Cu^{2+}, the EPR data quoted in [3] indicate that on the average there is less than one defect per excited MC. The Coulomb field of the RCC and the chlorine defects affects the excitons and causes their dissociation, which is the origin of the exciton dips in the spectrum in Fig. 2. The ratio of the exciton dip depth to the exciton band intensity in the initial absorption spectrum can serve as a rough estimate of the volume share of the activated MC: for glass samples 0.5 mm thick, this value is about 1/10. As the tinting relaxes, the number of RCC decreases and the dip depth becomes smaller. The fact that the lowest relaxation rate of all spectral bands correlates with the exciton dip is explained by the fact that the exciton dip tracks the field of all RCC. The Coulomb field also affects the electron levels of the dimensional quantization [6] of the MC, which causes the formation of an oscillating tail near the edge of the MC interzonal absorption (Fig. 3, spectrum *3*). Similar oscillations were registered in an external constant electrical field for the glasses with other types of MC.

Based on the data in Fig. 3, it is possible to infer the possibilities of photochromic glasses. As can be seen, no less than three types of RCC are formed in the glass under the effect of UV radiation, whereas the absorption band of only one of these types is fully overlapped by the range of spectral sensitivity of the human eye. This means that the photochromic effect for the "serviceable color center" $\leq 1/3$. Furthermore, since only the absorption band 16,000 cm^{-1} is "serviceable", the absorption of the activating radiation by the induced bands of glass RCC and chlorine defects of MC and the subsequent scattering of absorbed energy through lattice vibrations or the luminescence of chlorine centers further diminish the formation efficiency of the band at 16,000 cm^{-1}, i.e., decrease the efficiency of the photochromic effect in general.

Thus, the induced absorption spectra of photochromic copper-haloid glasses in the investigated wavelength range can be represented as the sum of absorption bands of three types of traditional radiation color centers of sodium-silicate glasses and two types of chlorine defects of CuCl microcrystal. The relaxation of these absorption bands is accompanied by a decrease in the depth of the exciton dip; in this way the microcrystal responds to the presence of the color centers. All the specified color centers are formed as the consequence of the absorption of a UV light quantum by the microcrystal and its surface states, trapping of generated vacancies on the chlorine defects, migration of the generated electrons toward the MC – glass border, their transition across this boundary, and trapping of the electrons by the glass lattice defects which are the predecessors of radiation color centers. The close arrangement of all resulting defects to each other and their interrelation with the microcrystal contribute to fast relaxation of induced pigmentation through the processes of recombination of carriers.

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